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14. ABSTRACT This report summarizes developments from November 2008. The original contract was aimed at the investigation of ion propulsion based on ionic liquids (ILs). The scope was widened with new funds (\$35,000 and \$50,000, received for 2008 and 2009, respectively) to study also colloidal propulsion (based on charged nanodrop beams rather than ion beams). This work would rely on electro sprays of mixtures of form-amide and propylene carbonate with selected ionic liquids. In our earlier report we explained the need to measure directly the activation energy $\Delta G$ for ion evaporation of ionic liquid anions and cations. The goal was to identify ILs for which $\Delta G$ is as high as possible, as this enables the production of small nandrops to achieve high specific impulse, without the simultaneous production of ions which would decrease propulsion efficiency.					
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# **Report on AFOSR award**

## **Title:**

**Efficient electrospray propulsion with widely variable specific impulse: Supplement  
to AFOSR grant FA9550-06-1-0104**

**FA9550-06-1-0104**

**Dr. Mitat Birkan program Manager**

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## STATUS OF EFFORT

A first focus has been the use of Yale's new facility for ion mobility mass spectrometry (DMA-MS: <http://www.eng.yale.edu/DMAMSfacility/>) to characterize nanodrops of ionic liquids, from which we infer the activation energy  $\Delta G$  for ion evaporation from neutral solvents. The Goal is to maximize this quantity to achieve the highest possible variable specific impulse in colloidal electrospray propulsion. Previous preliminary studies in a similar DMA-MS facility in Spain, gave  $\Delta G \sim 1.6$  eV for the ionic liquid (IL) EMI-Methide. Also taken in that visit but not analyzed in the prior report were data for three other ILs. Two of them, corresponding to large anions (EMI-Methide, EMI-Beti), gave comparably low  $\Delta G$ . The third, EMI-BF<sub>4</sub>, gave a similar  $\Delta G$  in positive ionization, yet a considerably higher value ( $>1.83$  eV) in negative mode. Yale's DMA-MS facility became operational on Jan/2009, and has enabled revising these initial data and studying several other ILs. Mr. Juan Fernandez-Garcia has found more favorable (larger)  $\Delta G$  values, approaching 1.9 eV (in positive and negative polarity) for ILs made up of small anions and cations [EMI-SCN, EMI-N(CN)<sub>2</sub>]. His new measurement of EMI-BF<sub>4</sub> confirms the earlier data, indicating the superiority of the two new ILs, and suggesting new studies with still smaller anions and cations.

In a second line of work co-sponsored by the Petroleum Research Fund, Mr. Carlos Larriba has studied electrosprays of the ionic liquid EMI-BF<sub>4</sub> immersed in a heptane bath rather than in vacuum. The ions and clusters of the IL formed drift immediately to the free surface of the heptane, producing a fine spray of heptane drops carrying within the charged particles of IL. The heptane then evaporates leaving the IL clusters free and unagglomerated in the gas phase. There we measure their mobility distribution, which reveals the presence of ions in a spectrum dominated by drops. The drop diameter decreases with flow rate achieving rather small diameters ( $<6$  nm). This new measurement technique is very informative (though not as much as DMA-MS), and technically much simpler than any previously tested alternative.

Initial explorations of colloidal propellants suitable for dual propulsion are reported based on the nitrate salt ethylammonium formate mixed with propylene carbonate.

With the few remaining resources we intend to investigate a few salts including the small cations acetate<sup>-</sup> and nitrate<sup>-</sup>, and the anions methylimidazolium<sup>+</sup>, and methylammonium<sup>+</sup>. In fact, the best specific impulse we have so far attained in colloidal propulsion is for formamide + methylammonium formate. In our earlier report (Nov/2008) we used a different (probably less precise) method to determine  $\Delta G = 2.16$  eV for ethylammonium formate in positive mode.



## **Index**

Status of effort	2
Index	3
1. Background	4
2. Measurement of $\Delta G$ in the new DMA-MS facility	4
3. Discussion on the most promising ILs for colloidal propulsion	9
4. Ion evaporation studies in a heptane bath	11
5. Dual propulsion based on ethylammonium nitrate	13
6. Personnel	14
7. Publications	15
8. Interactions/transitions	16

## 1. Background

This report summarizes developments from November 2008. The original contract was aimed at the investigation of ion propulsion based on ionic liquids (ILs). The scope was widened with new funds (\$35,000 and \$50,000, received for 2008 and 2009, respectively) to study also colloidal propulsion (based on charged nanodrop beams rather than ion beams). This work would rely on electrosprays of mixtures of formamide and propylene carbonate with selected ionic liquids. In our earlier report we explained the need to measure directly the activation energy  $\Delta G$  for ion evaporation of ionic liquid anions and cations. The goal was to identify ILs for which  $\Delta G$  is as high as possible, as this enables the production of small nanodrops to achieve high specific impulse, without the simultaneous production of ions which would decrease propulsion efficiency. We reported preliminary results obtained based on the measurement of the mobility and the mass/charge of ionic liquid nanodrops produced by electrospraying their solutions in acetonitrile at atmospheric pressure. Evaporation of acetonitrile leads to a continuous increase in the electric field on the drop surface. This process continues until the field is high enough to be relieved by evaporation of charge in the form of individual ions. Once the acetonitrile is completely evaporated, a nanodrop of involatile IL remains, whose charge is measured as a function of its radius. From this information and ion evaporation theory we infer a value of  $\Delta G$  for the dissolved IL. For positive and negative mode electrosprays, we obtain  $\Delta G$  values for evaporation of the positive and negative ion, respectively (Table 1). Progress on the identification of improved ILs based on the DMA-MS technique will be reported in section 2.

Table 1: Activation energies for positive and negative electrosprays of four ionic liquids. From [1]. The value for EMI-BF<sub>4</sub> in positive mode is revised in Table 2.

Ionic liquid	$\Delta G$ positive (eV)	$\Delta G$ negative (eV)
EMI-BF <sub>4</sub>	1.58 (1.68)	>1.83
EMI-Beti	1.54	1.65
EMI-Im	1.61	1.61
EMI-Methide	1.57	1.59

## 2. Measurement of $\Delta G$ in the DMA-MS facility for novel IL identification

Initial work was based on a visit to a facility in Spain combining a differential mobility analyzer (DMA) for mobility measurement, and a sophisticated time of flight mass spectrometer (TOF-MS) for mass/charge measurement. At the writing of our earlier report we were negotiating an 18 month loan to Yale of a similar facility. The negotiations have been successful, and Yale's new DMA-MS facility became operational on Jan/2009 (<http://www.eng.yale.edu/DMA-MSfacility/>). It will remain available at least until June 2010 according the existing 18 month loan agreement with the companies Applied Biosystems and SEADM. The agreement is renewable, and discussions with both manufactures to extend the loan have already started. The outcome of these negotiations will not affect our progress with the limited funds remaining under the current no-cost extension.

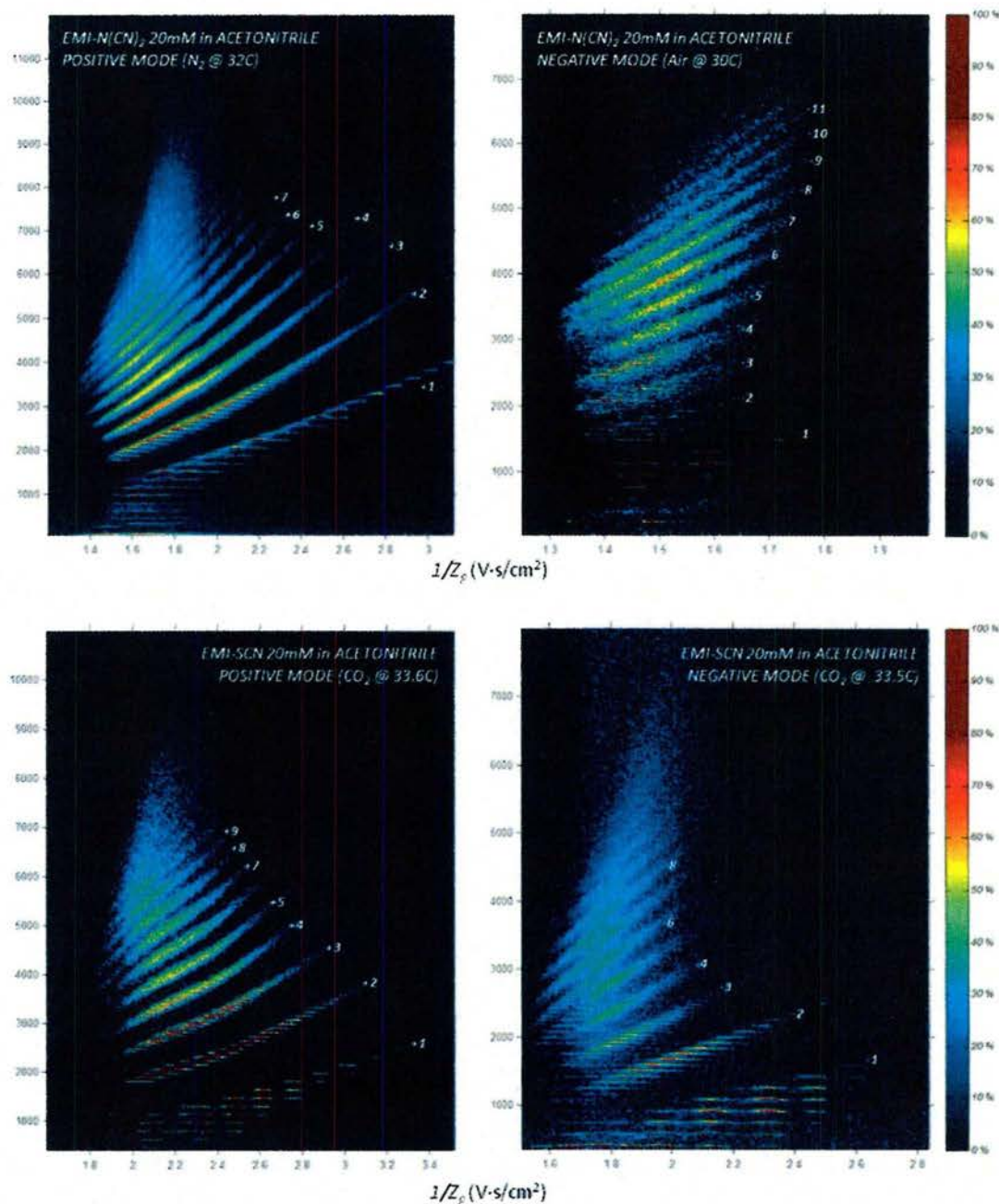


Figure 1: Mobility-mass spectrometry data from the ionic liquids EMI-C(CN)<sub>2</sub> (top) and EMI-SCN (bottom) in positive and negative and negative ionization

The facility was originally manned by Dr. Chris Hogan, whose stay at Yale was supported by SEADM. Dr. Hogan did all the initial work to develop the technique to measure  $\Delta G$ , and studied with it a first group of four commercially available ILs. Prior to the installation of the Yale DMA-MS instrument, in a one month visit to a similar facility in Spain, Dr. Chris Hogan measured a relatively low value  $\Delta G = 1.66$  eV for the ionic liquid (IL) EMI-Methide. Also taken in that visit but not analyzed in the prior report were



data for three other ILs. Two of them, corresponding to large anions (EMI-Im, EMI-Beti), gave comparably low  $\Delta G$ . Interestingly, EMI-Im was the propellant selected by Busek for their colloidal thruster for NASA's DR7 program. It was already clear that this propellant produces a substantial ion current even at relatively low specific impulse, so the modest  $\Delta G$  measured is not at all surprising (note that propulsion efficiency and specific impulse are not key issues in the DR7 and LISA programs). The third IL, EMI-BF<sub>4</sub>, gave a comparable  $\Delta G$  in positive ionization, yet a considerably higher value in negative mode. This provided a first indication of the advantages of small anions. These results have been published and the corresponding  $\Delta G$  values are listed in Table 1.

Table 2: Characteristics of two new ILs with smaller ions, and revision of EMI-BF<sub>4</sub> data.

<i>Liquid and Mode</i>	$\Delta G_s^o$ (eV)	<i>error (eV)</i>	<i>z range</i>
EMI-N(CN) <sub>2</sub> <sup>+</sup>	1.91	±0.025	3 - 9
EMI-N(CN) <sub>2</sub> <sup>-</sup>	1.86	±0.023	3 - 8
EMI-SCN <sup>+</sup>	1.86	±0.030	3 - 11
EMI-SCN <sup>-</sup>	1.865	±0.023	3 - 8
EMI-BF <sub>4</sub> <sup>+</sup> (Acetonitrile)	1.68	±0.035	3 - 12
EMI-BF <sub>4</sub> <sup>+</sup> (Methanol)	1.64	±0.013	5-9

After the departure of Dr. Hogan, this line of research has continued, now under AFOSR and Yale sponsorship. It has been carried out by a new Graduate student, Mr. Juan Fernandez-Garcia, previously involved in our AFOSR program while performing his senior project. In view of the apparent promise of small anions, we have investigated ILs made up of the smallest anions and cations for which they exist commercially [EMI-SCN, EMI-N(CN)<sub>2</sub>, EMI-BF<sub>4</sub>]. Figure 1 shows the two-dimensional spectra obtained for the first two ILs. The horizontal variable is the inverse mobility  $1/Z$  (in Vs/cm<sup>2</sup>). The vertical coordinate is the number of salt molecules  $n$  in the nanodrop divided by the number  $z$  of elementary charges, which is simply related to the mass over charge measured by the mass spectrometer. The plots show many broad bands with positive slope, made up of short horizontal segments at sharply defined masses. Each of these short horizontal segments corresponds to a nanodrop of exactly known composition (EMI) <sub>$z+n$</sub> (SCN) <sub>$n$</sub>  [or (EMI) <sub>$z+n$</sub> {N(CN)<sub>2</sub>} <sub>$n$</sub> ]. Each of the inclined lines is associated to a series of clusters in a fixed charge state  $q = ze$  involving  $z$  elementary charges (marked in the figure). The lowest inclined band corresponds to  $z = 1$ , with  $z$  values increasing upwards for successive bands. As one follows each band towards the left (decreasing cluster masses), the band eventually stops at a certain cluster having the minimum mass at which a nanodrop can hold  $z$  charges. At this point one charge evaporates in the form of the cation of the ionic liquid, with the corresponding cluster ion shifting to the right end of the lower charge state  $z-1$ .

This work has found improved  $\Delta G$  values, approaching 1.9 eV for both ILs (Table 2). Interestingly, this important advantage applies both in positive and negative polarity for EMI-SCN, EMI-N(CN)<sub>2</sub>, but only in negative mode for EMI-BF<sub>4</sub>, in agreement with the earlier findings of Dr. Hogan for EMI-BF<sub>4</sub> (although the earlier datum was 0.1 eV smaller than the new; Table 1, top of second column). This undesirable peculiarity of EMI-BF<sub>4</sub> remains to be explained.

**Effect of the solvent.** The two solvents used in these studies are appropriate for the DMA-MS technique because of their volatility, but are not appropriate for direct use in propulsion for that same reason. The effect of the solvent on  $\Delta G$  is believed to be small, but the activation energy tends to increase slightly with surface tension  $\gamma$ . Because  $\gamma$  is higher in solvents suitable for propulsion (formamide, FM and propylene carbonate, PC) than in acetonitrile or methanol, we have always intended to carry out these measurements in FM and PC. However, our efforts have been unsuccessful because these solvents are unavailable in sufficient purity. Hence, the ion impurities they contain distort the spectra shown in figure 1, precluding data inversion (i.e., too many foreign peaks blur the sharp bands). Fortunately, we have recently identified several solvents available in high purity (HPLC grade), and intend to study our most promising ILs in their corresponding solutions. The solvents are Dimethylformamide (DMF), N-Methyl 2-Pyrrolidone (NMP), and Dimethyl sulfoxide (DMSO). All of them have also high boiling points (202 °C for NMP), almost as high as PC and FM, which may make them also suitable for direct propulsion work. This opens also new possibilities for colloidal propellant optimization which we have no resources to address in the short term, but we hope to pursue in a future extension of this program.

A second important point where the change of solvent is relevant is in enabling extending towards larger drops the conditions under which  $\Delta G$  is measured, at sizes more directly applicable to colloidal propulsion. This may be seen in figure 2, which plots the number of charges in IL nanodrops versus mean drop radius, and includes also the Rayleigh limit charge, or maximum charge that a solvent drop can hold.

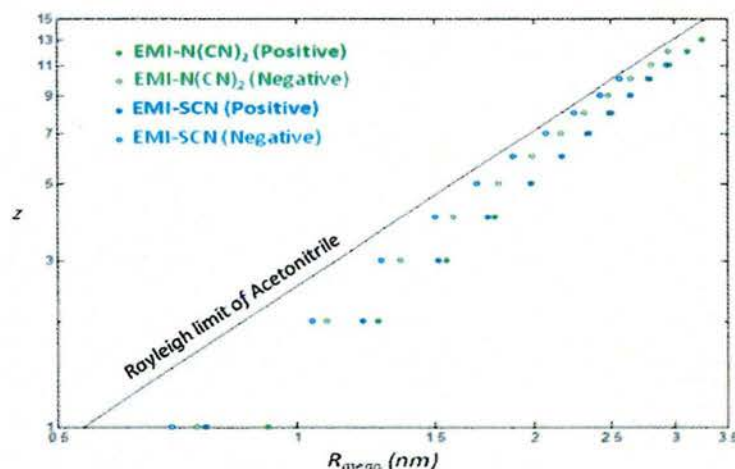


Figure 2: Number of charges in IL nanodrops versus mean drop radius for the two new ILs studied. The continuous lineshows the maximum charge that a solvent drop can hold.

**Development of software tools for fast analysis of DMA-MS spectra.** Our Initial spectra were interpreted manually, reading masses and mobilities for relevant peaks directly in DMA-MS spectra such as those in figure 1. As we have proceeded to analyze numerous similar series, we have been forced to automate the process. The development has been carried out very ably by Mr. Juan Fernandez Garcia under AFOSR support, with considerable help of Mr. Alejandro Casado of SEADM. The inversion is based on the known relation between mobility  $Z$ , charge state  $z$  and droplet diameter :  $Z \sim z/d^2$ , and the



trivial relation  $z(m/z) = \pi \rho d^3/6$ , where  $\rho$  is the bulk density of the IL forming the nanodrops. Knowledge of the pair of variables  $Z$ ,  $m/z$  enables the determination of  $z$ . We then transform the spectra from  $(m/z, Z)$  variables into  $(m/z, z)$  variables, as shown in figure 2. This then puts all ions into a  $z$  bin, which fixes  $z$  (as an integer) for all of the data, providing then  $m$ , and the exact composition. Indeed, the nanodrop is made of  $n$  ion pairs and  $z$  unpaired anions. Therefore its mass is  $m = n(m_+ + m_-) + zm_-$ , where  $m_+$  and  $m_-$  are the masses of the cation and the anion, respectively. The result is an ion abundance (included as the color scale of figure 1) as a function of  $n$  and  $z$  (or nanodrop radius and  $z$ ), which can be represented in the form of Figure 4. This figure is a direct confirmation of the ion evaporation mechanism, since each size distribution for a given  $z$  is to the left of the distribution for the charge state  $z+1$ , simply because evaporation of a single charge from a cluster holding  $z+1$  charges yields a cluster holding  $z$  charges. The smallest size that exists at a given  $z$  corresponds to the condition where the ion becomes unstable and evaporates that charge. This information coupled to ion evaporation theory yields the activation energy  $\Delta G$  directly and automatically from the graph, without any manual work other than verifying that the various charge state bins fall indeed in the close vicinity of an integer number, as they do in figure 3.

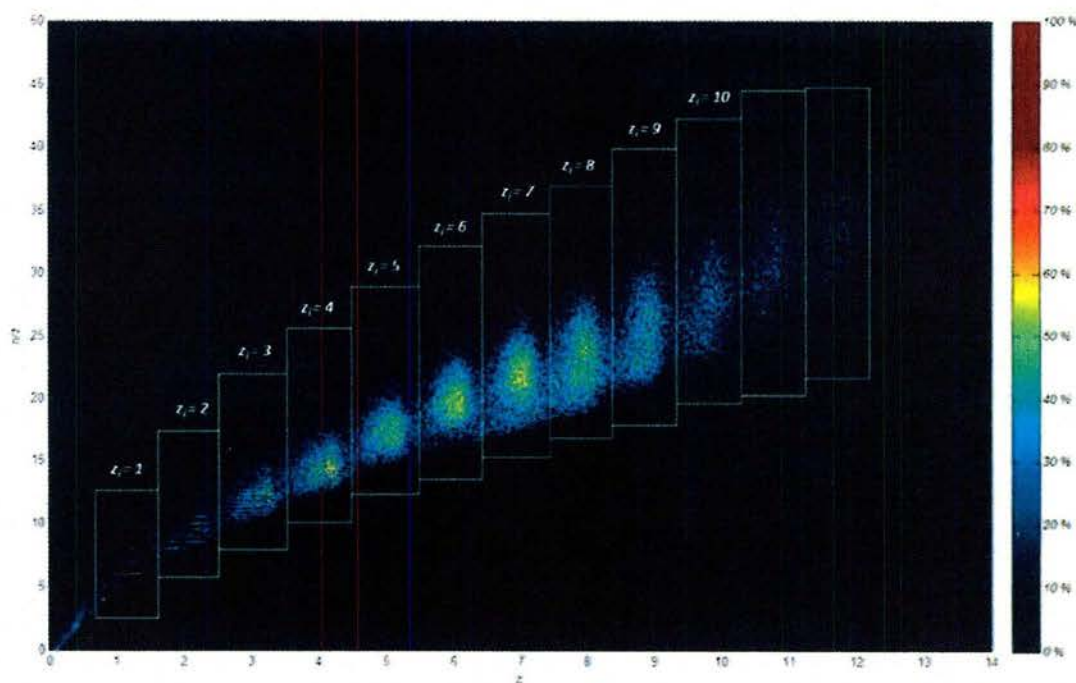


Figure 3. Transformation of figure 1b from  $(m/z, Z)$  variables into  $(m/z, z)$  variables for EMI-N(CN)<sub>2</sub> 20mM in acetonitrile (negative mode), showing how the various ions are grouped into vertical series according to their charge state.

### 3. Discussion on the most promising ILs for colloidal propulsion

1) Most conventional and widely used ILs are made up of large anions, have small  $\Delta G$  values and are inadequate for colloidal propulsion.

2) There are a few exceptions of ILs with relatively small cations, which we have studied in some detail.

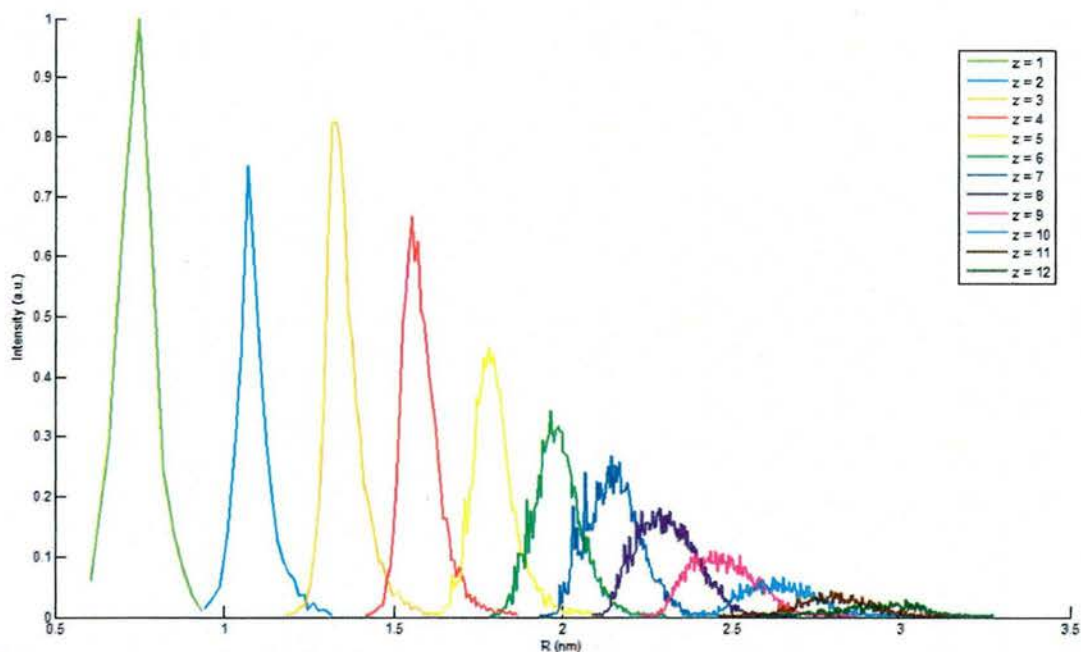


Figure 4: Abundance versus radius for nanodrops of given charge state. EMI-N(CN)<sub>2</sub> 20mM in acetonitrile in negative mode.

- i) EMI-BF<sub>4</sub> has been widely used in electrospray propulsion, and does indeed exhibit an increased  $\Delta G$  in negative mode. Even so, its positive mode  $\Delta G$  is too small making it non-ideal for colloidal propulsion.
- ii) The best combination of anions and cations obtained in commercially available ILS is given by the EMI cation paired with the relatively small anions SCN<sup>-</sup> and N(CN)<sub>2</sub><sup>-</sup>, both approaching  $\Delta G = 1.9$  eV in both polarities. A more detailed examination of their performance shows a slight advantage of EMI-SCN in negative mode, though its propulsive performance has not yet been studied directly. Of these two salts, the least favorable is EMI-N(CN)<sub>2</sub> in positive mode. We have already studied its propulsive performance in formamide and PC mixtures. It is inferior to that obtained with more compact salts such as methylammonium formate.
- 3) Pending direct measurement of the propulsive characteristics of EMI-SCN, this salt is clearly the best among conventional (non-volatile) commercial ILS. Nonetheless, we believe however that even better candidates can be found.
- 4) One open option for such improvements is shifting to unusual families of ILS. In these we include ILs which had been previously rejected due to some unfavorable such as (i) a high viscosity, (ii) a melting point above room temperature, or (iii) a finite volatility.
  - i) This option involves the use of molecular anions such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>. The corresponding EMI<sup>+</sup> salts melt between 79 and 89 °C, but freeze only between 30 and



39 °C.<sup>1</sup> These ILs had never been used in propulsion applications due to their very high viscosity (> 1000 cp), until Lozano boldly introduced them iodide as a source of atomic ion beams. It is indeed amazing that such extremely viscous materials can form Taylor cones operating in the purely ionic regime, but they do. For colloidal applications we had rejected them due to the conviction that their extreme viscosity would limit too much the conductivity attainable in mixtures of FM or PC. However, Lozano's precedent gives some hope of success. One would also expect exceptionally high  $\Delta G$  values in association with the small atomic cations involved. These combinations therefore deserve serious consideration, both, through the measurement of  $\Delta G$ , and through direct analysis of their propulsive performance in FM and PC mixtures.

ii) There are of course many other salts such as ClNa whose anions and cations are both tiny. The problem is that they have large melting points. There are nonetheless some workable compromises of salts with smaller ions than those so far tested, and with melting points only slightly above room temperature. We list some interesting examples. The dimethyl imidazolium cation (**DMI**<sup>+</sup>), is smaller than EMI, yet its N(CN)<sub>2</sub> salt melts only slightly above room temperature (34 °C). We have already received samples of DMI-N(CN)<sub>2</sub> from Prof. Y. Yoshida, and studied the propulsive properties of DMI-N(CN)<sub>2</sub> in the purely ionic regime, which are exceptional. We have also analyzed the propulsive performance of this salt in formamide mixtures, and obtained promising results, but still inferior to the best achieved. Many other combinations of this cation are possible which may be superior to those already tested. We will continue investigating them as they are synthesized by others. Another example is given by the relatively small anion NO<sub>3</sub><sup>-</sup>, which is of extra interest because many of its salts are energetic materials suitable also for chemical propulsion. The melting point of EMI-NO<sub>3</sub> is only 313 K.<sup>2</sup> A number of partially volatile salts based on the nitrate ion will be discussed below.

iii) There is finally a large family of salts based on reactions between acids and amines yielding salts whose cation is the protonated amine:



The use of these salts has been limited (relative to conventional involatile ILs) due to their finite volatility. This feature is associated to the slight reversibility of reaction (1), which yields a small fraction of acid and amine, both of which are volatile. Still, this volatility is often modest comparable to that of FM and PC, hence tolerable in propulsion applications. One could even argue that this small level of volatility is desirable to avoid permanent short-circuits when there is a propellant spill. The best colloidal performance we have so far achieved is in fact for a mixture of formamide with a salt of type (1), combining formic acid with methylamine. In our earlier report (Nov/2008) we described the PhD work of Mr. Sergio Castro using a different mass spectrometric technique (pure MS without DMA) to determine  $\Delta G > 2.16$  eV for methylammonium formate and ethylammonium formate in positive mode (Table 1). He also analyzed several chemically similar salts, including triethylammonium acetate, having a larger cation, resulting in  $\Delta G$

<sup>1</sup> Ngo, H. L.; LeCompte, K.; Hargens, L.; McEwen, A. B., Thermal properties of imidazolium ionic liquids, *Thermochim. Acta* 357-358, 97-102, 2000

<sup>2</sup> Hu Cang, Jie Li, and M. D. Fayer, Orientational dynamics of the ionic organic liquid 1-ethyl-3-methylimidazolium nitrate, *J. chem. Phys.* 119(24), 13017-13023, 2003



= 1.91 eV in positive mode. However, when interpreting similar measurements by Hatreux using the same method he found  $\Delta G = 1.73$  eV, suggesting that the approach needs to be reexamined. The experimental technique is based on measuring the charge remaining on a protein of known size after electrospraying it from an aqueous solution containing the IL. Triethylammonium acetate has now been studied more carefully by Dr. Hogan using protein residue ions by the DMA-MS technique [2], leading to  $\Delta G = 1.78$  eV. The new datum is more reliable than the old as it is based on a large number of proteins of different sizes. We have very recently also analyzed this salt via DMA-MS and found that the technique is still viable in spite of its modest volatility.

**Table 1:** Energy of evaporation of several IL cations from water (S.Castro, PhD Thesis).

Ionic liquid	Ion selected	$z_{\min}-z_{\max}$	$\Delta G$ (eV)
Diethylammonium formate	Diethylammonium	6	2.00
Ethylammonium formate	Ethylammonium	7-8	2.16-2.30
Methylammonium formate	Methylammonium	7-8	2.16-2.30
Triethylammonium acetate	Triethylammonium	4.5	1.91

Two main reasons make partially volatile ILs promising for colloidal propulsion. First, liquid salts can be formed with smaller cations and anions than in conventional ILs. The anions include small amines such as methylamine and the cations may be as tiny as acetate and nitrate. Second, some of the volatile nitrate salts just mentioned have promising characteristics both as electrospray propellants and as chemical propellants. Most notable is the case of ethylammonium nitrate,<sup>3</sup> which we have already studied in mixtures with PC. It is quite promising, though not so much as methylammonium formate. These data are discussed further in section 5 on dual propulsion.

**New ILs to be studied in the immediate future.** The preceding discussion shows that many options remain to be explored. However, given the limited resources available, we will focus on just a few. In particular, we wish to determine  $\Delta G$  values for the smallest ions mentioned, including as many as we can handle among: formate<sup>-</sup>, acetate<sup>-</sup>, nitrate<sup>-</sup>, dimethylimidazolium<sup>+</sup>, ethylammonium<sup>+</sup>, methylammonium<sup>+</sup>, and the halides Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>.

#### 4. Ion evaporation studies in a heptane bath

Mr. Carlos Larriba was previously supported by this grant, to which he made important contributions. He is presently funded by a related grant from the Petroleum Research Fund (PRF) of the American Chemical Society. The goal is to study ion injection from the Taylor cone of an ionic liquid into an insulating liquid such as heptane. The phenomenon is conceptually similar to our AFOSR program, except that the vacuum environment is substituted by a dielectric liquid. It would have been more convenient to substitute the vacuum by atmospheric air, but this is precluded by the evaporation of ions in the presence of strong electric fields (1 V/nm), which provides them with an energy of the order of 60 eV before their first collision with a gas molecule (1 mean free path ~60 nm). This energy leads to secondary ionization of the gas and possible fragmentation and charge reduction of the ions coming from the IL tip. These extraneous phenomena distort

<sup>3</sup> P. Walden, Bull. Acad. Imper. Sci. (1914)



the composition of the IL nanodrops greatly complicating their study. In the heptane bath, however, the mean free path is of atomic dimensions, and the ejected ions do not attain ionizing collisions. Whatever ions and nanodrops are injected in the dielectric liquid are preserved as produced, and can therefore be studied. The experimental methods under atmospheric pressure are of course much simpler than under vacuum, so the project permits making independent and simplified progress into essentially the same basic problem (though under different conditions leading evidently to quantitatively different results). One of the studies we have carried out consist on injecting an electrospray of EMI-BF<sub>4</sub> into heptane, and in turn atomizing the heptane into drops that evaporate leaving into the gas the same IL nanodrops and ions that were injected into the liquid. These we may then analyze with a variety of experimental techniques. We have attempted to do so in the DMA-MS system, but ion transmission turns out to be insufficient to see anything other than the dimer ion (EMIBF<sub>4</sub>)EMI<sup>+</sup>. The problem is that the heptane drops are much larger than the acetonitrile drops used in the other DMA-MS study, so we need to give time for them to evaporate. This forces us to remove the drop source to a certain distance from the inlet to the instrument, which dilutes the signal to the low levels noted. Still, the identification of the dimer ion in the MS leaves no doubt regarding the fact that the Taylor cone of the IL is injecting ions into the heptane, very much as it does under vacuum conditions.

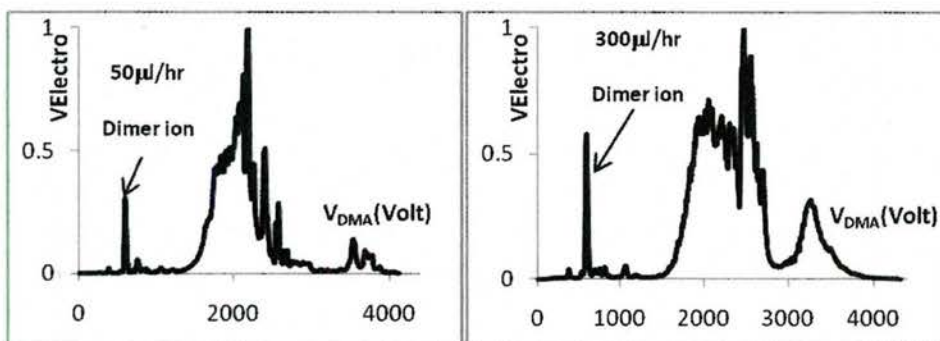


Figure 5: Mobility distribution of EMI-BF<sub>4</sub> nanodrops and ions produced by electrospraying the IL inside a heptane bath. The DMA voltage shown is inversely proportional to mobility in air.

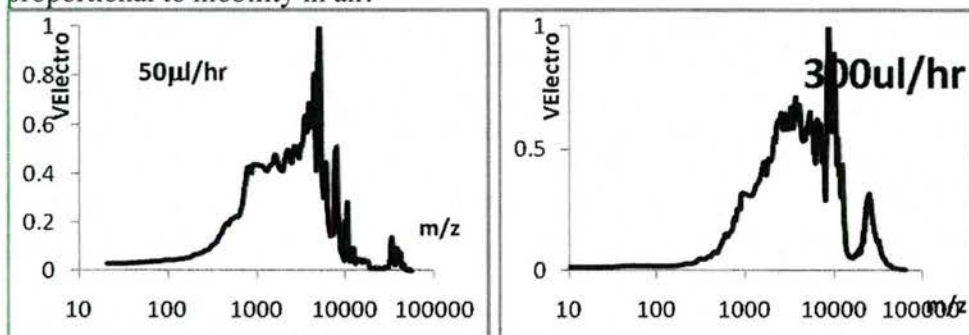


Figure 6: m/z (Da) distribution of EMI-BF<sub>4</sub> nanodrops (excluding ions) obtained from the data of figure 5 and the assumption that the drops are charged to 50% of the Rayleigh limit in the heptane bath.

In view of the insufficient sensitivity of the MS, we have carried out experiments with the DMA alone, using an electrometer as the detector. From these we obtain distributions of mobilities (in air) of the IL nanodrops, such as those shown in figure 5. In these figures the voltage scale is directly proportional to the inverse mobility of the ions in air. The mobility scale is known from the known mobility of the dimer ion, whose identity we have confirmed in the DMA-MS experiments already mentioned. From these mobility distributions and the assumption that the IL drops are charged to 50% of the Rayleigh limit we may infer distributions of  $m/z$  (hence propulsive characteristics if the same nanodrops were produced in vacuo), drop size, charge, etc. For instance, Figure 6 shows  $m/z$  distributions for the data of figure 5. Interestingly, mean drop diameters based on the highest peak in figure 5 are smaller than 5 nm.

### 5. Dual propulsion based on ethylammonium nitrate

We have previously noted the interest of nitrate based ILs for dual (electrical-chemical) propulsion. We have identified two promising nitrates with melting points near or below room temperature: EMI-NO<sub>3</sub> and ethylammonium nitrate. We have also explored the colloidal propulsion characteristics of the later, as part of the Ph.D. Thesis of Mr. David Garoz (to be defended before the summer of 2010). It contains a large number of data on colloidal propellants, tested directly in a vacuum, and analyzed via time of flight mass spectrometry (TOF-MS). TOF curves for ethylammonium nitrate mixed in varying proportions with PC are shown in figure 7. The  $I_{sp}$  value shown in the bottom figures is based on an acceleration voltage of 1600 V. Post acceleration to 10 kV would give a maximum  $I_{sp}$  of 2000 s, though at a limited propulsion efficiency.

This work is preliminary and samples a rather small piece of a rather large field. The literature on energetic ionic liquids is growing rapidly, and extends well beyond the possibilities afforded by imidazole, including salts based on the tetrazole and triazole rings among others.<sup>4</sup> The systematic development of dual propellants will require a substantial effort in collaboration with specialists on energetic ionic liquids. As an entry

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<sup>4</sup> G. Drake, G. Kaplan, L. Hall, T. Hawkins, J. Larue A new family of energetic ionic liquids 1-amino-3-alkyl-1,2,3-triazolium nitrates, *J. Chem. Crystallog.* 37(1), 15-23, 2007; GH Tao, Y Guo, YH Joo, B Twamley, JM Shreeve, Energetic nitrogen-rich salts and ionic liquids: 5-aminotetrazole (AT) as a weak acid, *J. Mater. Chem.*, 2008, 18, 5524–5530; AR Katritzky, H Yang, D Zhang, K Kirichenko, M Smiglak, JD Holbrey, WM Reichert; RD Rogers, Strategies toward the design of energetic ionic liquids: nitro- and nitrile-substituted N,N0-dialkylimidazolium salts, *New J. Chem.*, 2006, 30, 349–358; T Abe, GH Tao, YH Joo, RW Winter, GL Gard, JM. Shreeve, 5-(1,2,3-Triazol-1-yl)tetrazole Derivatives of an Azidotetrazole via Click Chemistry, *Chem. Eur. J.* 2009, 15, 9897-9904; TM. Klapötke, C Miro' Sabate, 5-Aminotetrazolium 5-Aminotetrazolates -New Insensitive Nitrogen-rich Materials, *Z. Anorg. Allg. Chem.* 2009, 635, 1812-1822; TM Klapötke, C Miró Sabaté, A Penger, M Rusan, JM Welch, Energetic Salts of Low-Symmetry Methylated 5-Aminotetrazoles, *Eur. J. Inorg. Chem.* 2009, 880–896; RP Singh, RD Verma, DT Meshri, JM Shreeve, Energetic Nitrogen-Rich Salts and Ionic Liquids, *Angew. Chem. Int. Ed.* 2006, 45, 3584 – 3601; N Fischer, K Karaghiosoff, TM Klapötke, J Stierstorfer, New Energetic Materials featuring Tetrazoles and Nitramines- Synthesis, Characterization and Properties, *Z. Anorg. Allg. Chem.* 2010, 636, DOI: 10.1002/zaac.200900521; MW Schmidt, MS Gordon, JA Boatatz, Triazolium-Based Energetic Ionic Liquids, *J. Phys. Chem. A* 2005, 109, 7285-7295



into that field, in collaboration with Professor R. Yetter, we have recently decided to test the electrospray performance of HAN-based solutions, both at atmospheric pressure (to determine  $\Delta G$  via DMA-MS) and in vacuum. It is unclear if HAN will remain liquid under vacuum, but because it is of current interest to the AFOSR, it makes sense to determine first its suitability for electrical propulsion prior to investigating other substances. Professor Yetter will in turn examine the energetic properties of ethylammonium nitrate and its mixtures with selected organic solvents.

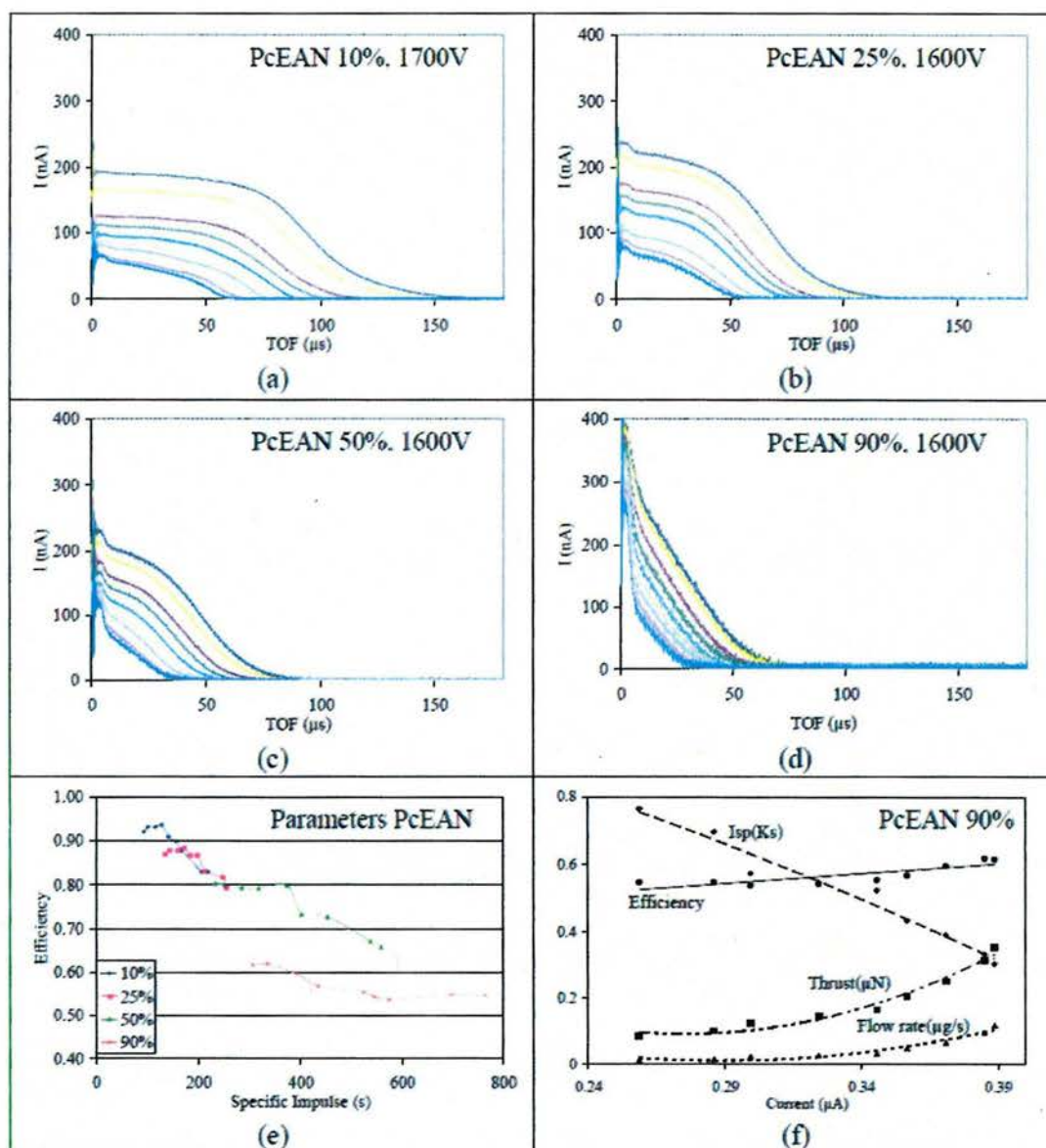


Figure 7: Characteristics of electrosprayed mixtures of PC with varying concentrations of ethylammonium formate. (a-d): TOF spectra. (e-f) propulsive characteristics.

## 6. Personnel Supported/or associated with the research effort.

**Faculty:** Prof. Juan Fernandez de la Mora, PI; Prof. Paulo Lozano, (MIT); Prof. Rich Yetter (Penn state); Prof. Y. Yoshida (collaborator formerly at Kyoto University, now at Meijo University, Nagoya Japan); Prof. Chris Hogan (collaborator, University of Minnesota)

**Graduate students:** Carlos Larriba, Juan Fernandez-Garcia

**Postdoctoral fellows:** Dr. Chris Hogan, funded by SEADM, and working at Yale from September to July 2009.

#### **7. Publications acknowledging support from this grant**

- 1 C. J. Hogan Jr. & J. Fernández de la Mora, Tandem Ion Mobility-Mass Spectrometry (IMS-MS) Study of Ion Evaporation from Ionic Liquid-Acetonitrile Nanodrops; *Phys. Chem. Chem. Phys.*, 2009, 11, 8079-8090.
- 2 C. J. Hogan Jr. & J. Fernández de la Mora, Ion Mobility Measurements of Non-Denatured 12-150 kDa Proteins and Protein Multimers by Tandem Differential Mobility Analysis-Mass Spectrometry (DMA-MS), submitted to *J. Am. Soc. Mass Spectr.*, 12/Jan/2010
- 3 B. K. Ku and J. Fernandez de la Mora, Relation between Electrical Mobility, Mass, and Size for Nanodrops 1-6.5 nm in Diameter in Air, *Aerosol Sci. & Techn.*, **43** (3), 241-249, 2009
- 4 S. Castro and J. Fernandez de la Mora, Effect of tip curvature on ionic emissions from Taylor cones of ionic liquids from externally wetted tungsten tips, *J. App. Phys.*, **105**, 034903, 2009
- 5 Carlos Larriba-Andaluz and Juan Fernández de la Mora, Electrospraying insulating liquids by charged nanodrop injection from the Taylor cone of an ionic liquid, *Phys Fluids*, accepted for publication, 2010
- 6 S. Castro, Ionic emission from Taylor cones, Ph.D. Thesis, Yale University, Presented November 2008 (May 2009)

#### **Articles in preparation**

1. J. Fernandez-García, C. Larriba and J. Fernandez de la Mora. Electrospray emissions of ions and nanoclusters from two imidazolium ionic liquids based on the dicianamide anion.
2. C. Larriba, J. Fernandez-García and J. Fernandez de la Mora. Ion evaporation of relatively large clusters from Taylor cones of ionic liquids.
3. C. Larriba, J. Bango and J. Fernandez de la Mora, Effect of radiation on the electrospray propulsion characteristics of several ionic liquid propellants.
4. D. Garoz and J. Fernández de la Mora, electrical propulsion with electrosprayed nanodrops of formamide and propylene carbonate mixed with ionic liquids.
5. C. J. Hogan Jr. & J. Fernández de la Mora, Ion-Pair Evaporation from Ionic Liquid clusters, submitted to the *Journal of the American Society for mass spectrometry*, Jan/2010.
6. C. Larriba, C. Hogan and J. Fernandez de la Mora, measurement of the surface tension of single polymer molecules, in preparation, 2009
7. C. J. Hogan Jr., J. Fernández-García, & J. Fernández de la Mora. A wide mobility standard for calibration of non-linear IMS-MS instruments based on the Mobility-Size Relationship for electrosprayed nanodrops of ionic liquids



8. C. Larriba; On the “Surface” Tension of Organic and Inorganic Salts, manuscript under preparation

#### 8. Interactions/Transitions:

a. **Participation/presentations at meetings, conferences, seminars, etc.** As in 2008, in 2009 we participated at the Annual meeting of American Society for mass spectrometry, where Dr. Hogan and the PI presented two papers featuring the DMA-MS technique for analysis of IL nanodrops. Mr. Larriba and Mr. Fernandez-Garcia presented two papers involving electrosprays of ionic liquids at the Annual conference of the American Association for Aerosol Research. The PI presented a plenary lecture also featuring results from the DMA-MS analysis of nanodrops to the European Aerosol Association (Karlsruhe, October 2009). Shortly after, Dr. Hogan gave a similar talk to the Mechanical Engineering Department at the University of Minnesota.

c. **Transitions.** Describe cases where knowledge resulting from your effort is used, or will be used, in a technology application. Transitions can be to entities in the DoD, other federal agencies, or industry. Briefly list the enabling research, the laboratory or company, and an individual in that organization who made use of your research.

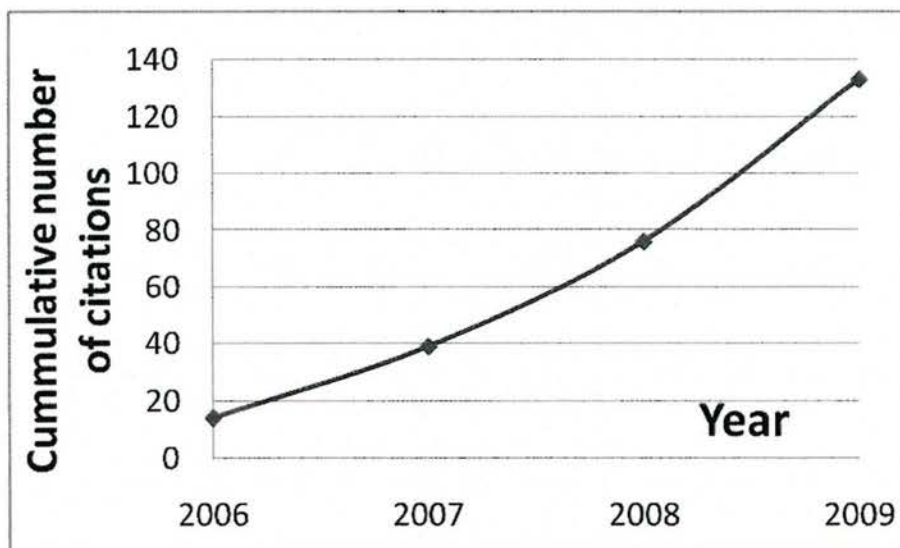


Figure 8: Number of citations in refereed scientific Journals of our 15 published articles relating to ionic liquid propulsion, totaling 133 over the last four years

As shown in figure 8, our work on ionic liquid propulsion is being cited and used increasingly by many other groups. The total number of citations received by the 15 articles we have published on ionic liquid propulsion is presently 133, and is growing very fast. Note that this figure does not include all citations to all our papers acknowledging AFOSR sponsorship, but only to those relating directly to propulsion based on IL liquids. The total is close to 200. This is unusual given the rather recent discovery of the propulsive usefulness of ILs, and the few groups working in this area in the US (MIT, JPL, Busek, CAC, Hanscom, J. Daly, M. Gamero, Yale) and more recently in Europe (led respectively by HR Shea in Switzerland and J Stark in the UK). All have embraced the

use of ionic liquid based propellants. Note that the majority of the propulsive studies making use of our findings on ionic liquid propellants are not published in Journal articles, but appear rather in conference publications such as those from the AIAA joint propulsion conferences not accounted for in figure 10. One example of such transitions is an excellent article by P. Lozano (MIT) on ILIS with porous emitters, based on new ILs we had supplied to him.

The European groups have so far worked only with EMI-BF<sub>4</sub>. It is very significant that all of the electrospray propulsio studies published so far have relied either on liquid metals, or on alternative propellants first developed by our group.

**9. New discoveries, inventions, or patent disclosures.** None.

**10. Honors/Awards:** None